Numerical Study of the Self-ignition of Tetrafluoroethylene in a 100-dm^3-reactor

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Abstract: Simulations were carried out with the aim of studying the self-ignition of tetrafluoroethylene initiated by contact with the hot walls of a 100-dm^3-reactor. The free convection caused by the exothermal reactions triggered by the contact with the hot reactor walls and the consequent self-heating of tetrafluoroethylene is simulated. For each initial pressure considered (5, 10 and 20 bar) various computations were performed, in order to assess the lowest wall temperature at which the heat produced by the on-going reactions cannot be dispersed to the surroundings. This temperature was defined as the ignition temperature for a specific initial pressure in the analyzed reactor. The results of the computations performed were compared with experimental data for the model validation, showing a good agreement.

**Keywords:** self-ignition, tetrafluoroethylene, large-scale reactor

1 Introduction

The self-ignition of tetrafluoroethylene (TFE) caused by contact with hot surfaces has been analyzed with the help of simulations performed with COMSOL Multiphysics®. The current study focuses on large-scale heated reactors for the industrial production of polytetrafluoroethylene (PTFE) from TFE at high pressures. Under undesired circumstances (e.g. wrong filling, failure of temperature control) gaseous TFE in contact with the hot walls may start to dimerize exothermically into octafluorocyclobutane (OFCB):

$$C_2F_4 \rightarrow 0.5 \ c\text{-}C_4F_8 \qquad \text{[Eq. 1]}$$
$$\Delta H_R = -105 \text{ kJ/mol} \qquad \text{(TFE Dimerization)}$$

Possibly, the energy released can heat up the gas phase to a temperature at which TFE decomposes in carbon black (soot) and tetrafluoromethane, as shown in [Eq. 2]. The decomposition reaction, once triggered, runs explosively and can result in the vessel rupture with consequent economical and eventually human losses.

$$C_2F_4 \rightarrow CF_4 + C \qquad \text{[Eq. 2]}$$
$$\Delta H_R = -257 \text{ kJ/mol} \qquad \text{(TFE Decomposition)}$$
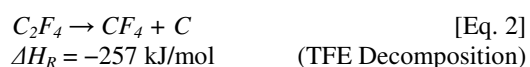
Simulations of the self-heating and consequent self-ignition of TFE in a 100-dm^3-reactor were carried out. The current paper describes the numerical model employed in the computations and reports on the achieved results.

2 Motivation

This study originally started by the initiation of a research project subsidized by an industrial association, PlasticsEurope, to improve the safety in PTFE producing factories. The aim of the study was to determine the MITD for TFE at elevated condition and to create a numerical model which is capable of simulating the self-heating process of TFE. The last phase of the research project consisted in validating the model with comparison with large-scale tests.

3 Background

The ignition properties of flammable gases in mixture with air are determined at atmospheric pressure with a special test procedure according to EN 14522 [1]. Here the concentration of the flammable gas in the mixture is varied and the minimum temperature when an ignition by hot walls takes place is determined. This temperature is called the Auto Ignition Temperature (AIT aka. MIT).

Nonetheless, gases like TFE can react explosively without the presence of oxygen or another oxidizer. For these gases, known as chemically unstable gases, no standards are defined for the assessment of the ignition triggered by hot walls. Therefore a similar concept was introduced, the Minimum Ignition

Temperature of Decomposition (MITD). This is defined as the lowest temperature of a hot surface at which self-ignition for the decomposition of a chemically unstable gas like TFE occurs without the presence of an oxidizer like air. Since most chemically unstable gases show their explosive behavior only at pressure above atmospheric conditions, test to determine the MITD are performed in closed pressure resistant vessel.

Experiments to determine the MITD of TFE at elevated pressures in small-scale apparatuses are reported in [2]. Furthermore, in a previous paper the self-heating of TFE in a closed vessel using a simple reversible reaction was described [3]. The model was then improved with a more complete reaction net and validated against small scale data in [4]. In the current paper the improved model is validated for large scale vessels.

4 Numerical Model

COMSOL® Multiphysics® [v3.5 to v4.2] was employed to model the problem. Three application modes of the *Chemical Engineering Module* were linked. The *non-isothermal flow mode (chns)* was used to describe the free convection caused by differences in densities in the system. These differences arise due to occurrence of the exothermic dimerization reaction, which is initiated at the vessel walls. The *convection and conduction mode (chcc)* was used to model the heat transfer resulting from the extended reaction net shown in Figure 1: beside the exothermic dimerization reaction [Eq. 1] and the endothermic back reaction [Eq. 3], four additional reactions were considered.
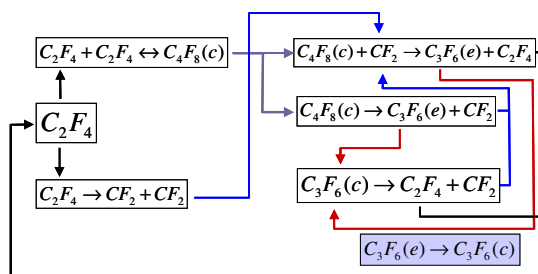
$$c\text{-}\ C_4F_8 \to 2\ C_2F_4 \qquad\qquad [\text{Eq. 3}]$$
$$\Delta H_R = 206\ \text{kJ/mol} \qquad\qquad (\text{OFCB decay})$$

Figure 1: Extended reaction net [5].

To close the equation system, the *convection and diffusion mode (chcd)* was used to model the mass balance by linking the reaction kinetics.

The model governing equations are summarized in Table 1. When considering the complex reaction net from Figure 1, there are nine unknown dependent variables.

The meshes used in the calculations are shown in Figure 2. Due to the symmetry of the problem, a 2D geometry using the axial symmetry modus was used if the vessel was vertically orientated. For the horizontally orientated vessel the problem is no more symmetrical, 3D simulation would be needed. In order to save computing times simulations on a xy-plane of a slice of the vessel were performed. This arrangement is acceptable since the length of the vessel is considerably larger than its diameter and thus the heat transfer along the z-direction can be neglected. The average quality of each mesh was always higher than 0.85.
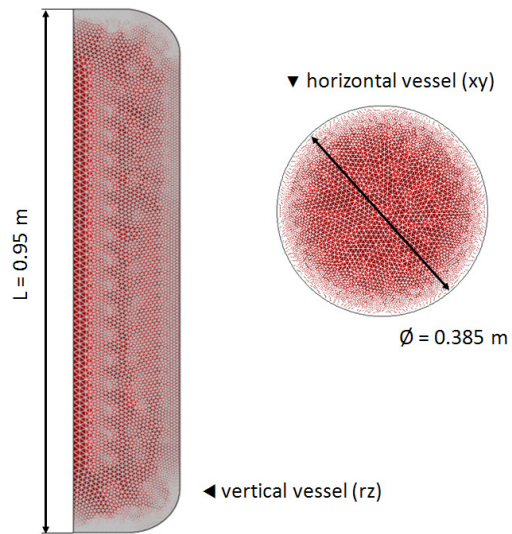

Figure 2: Meshes used in the calculations.

This model mainly consists of a gas domain that is surrounded by the fixed reactor walls at a constant temperature. The only gas domain is simulated. There is no inlet or outlet, because a prefilled closed vessel is modeled. The applied boundary conditions are shown in Table 2. The material properties have been taken from literature [8,9].

5 Experimental Setup

As to provide data for the model validation a new facility was assembled to perform ignition tests of TFE in a 100-dm^3-reactor. Figure 3 shows a sectional view of the vessel employed. In order to appreciate the effect of the orientation on the MITD of TFE, the reactor was mounted in a special support, which allowed for a free 360° rotation (see Figure 4).

Before each experiment the vessel was evacuated and then heated to the desired initial temperature. Then, TFE was filled to the defined initial pressure. The inlet was closed and pressure and temperature inside the vessel were recorded. If a peak in the pressure and temperature curves was observed, this was defined as an ignition. For each initial pressure tests were repeated, where the temperature was varied in steps of ± 10 K, until the lowest temperature leading to an ignition was detected. This temperature is the MITD for the specific initial pressure in the 100-dm^3-reactor. One experimental series pro vessel orientation (horizontal and vertical) was carried out.
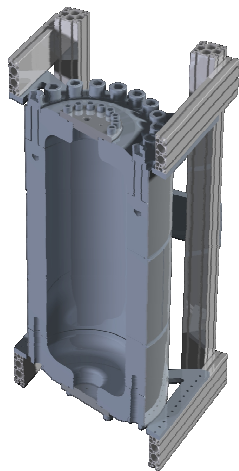

Figure 3: Sectional view of the 100-dm³-vessel used for the experiments to determine the MITD for TFE.

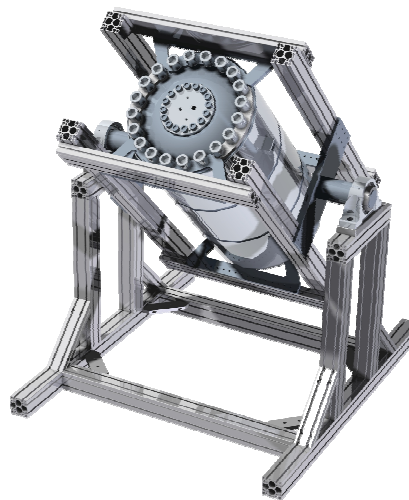Further details on the experimental setup can be found in [6] and [7].

Figure 4: 100-dm³-vessel mounted in a special rack allowing 360° rotation.

6 Results and Discussion

6.1 Experimental results

Table 3 presents the values of MITD of TFE collected during the current experimental campaign. It can be noticed that the effective initial pressure in the reactor exceeded the set pressure. In fact, during the tests cold gas was filled in the hot reactor and since the supply was stopped the moment the data acquisition system registered the set pressure, a higher amount of gas than required was actually filled. Since TFE behaves as in ideal gas at high temperatures in the pressure range of interest (according to [6] the real gas factors of TFE are close to 1), the ideal gas law was used to determine the real initial pressure.

The results in Table 3 show that the MITD of TFE decreases with increasing initial pressure, a fact which agrees with previous tests in small scale [2]. For what concerns the effect of the reactor alignment, differences in the MITD of TFE of max. 20 K within the pressure range analyzed were observed between the vertical and horizontal adjustment. Lower values of MITD were registered with the reactor in the vertical position. This is caused by the formation of local hot spots near the vessel top caused by buoyancy of hot reaction gases, which can enhance the initiation of the decomposition. The effect of the reactor arrangement seems to decrease as the initial pressure increases.

6.2 Simulation results

The simulated temperature distribution in the gas phase some seconds after the filling of TFE is presented in Figure 5 for a vertically orientated reactor. The formation of hot zones generated by the buoyancy effect caused by the local temperature differences due to the heat generation by the dimerization reaction is shown. For the vertically orientated vessel the buoyancy effect is stronger and this causes a larger heat accumulation at the reactor top, which can promoted side reaction and enhance the possibility of occurrence of an ignition, as experimentally confirmed by the achievement of lower MITDs (Table 3).
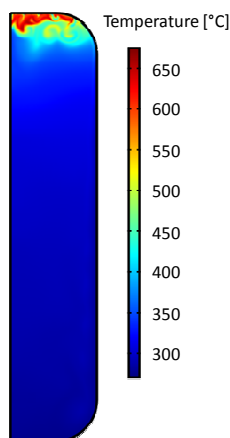

Figure 5: Temperature field in the 100-dm^3-reactor 30 seconds after the filling with an initial pressure of 10 bar and a constant wall temperature of 270 °C [vertical orientation].

Figure 6 shows the pressure-time curves achieved in simulations with an initial pressure of 6 bar and variable wall temperatures for the vertically orientated vessel. For an initial wall temperature of 230 °C the overall energy release by the on-going reactions causes only a limited pressure increase. Nonetheless, as TFE is further consumed the heat generated can be dissipated to the surrounding and no runaway is observed. If the wall temperature is increased to 240 °C a pressure peak is detected, meaning a runaway and therefore an ignition is observed. A further increase of the wall temperature causes a reduction in the induction time to the ignition in agreement to the experimental observation. For the specific case presented in Figure 6, the MITD

predicted by the model would be 240 °C, since this is the first temperature value in a range ±10 K, where an ignition is predicted.
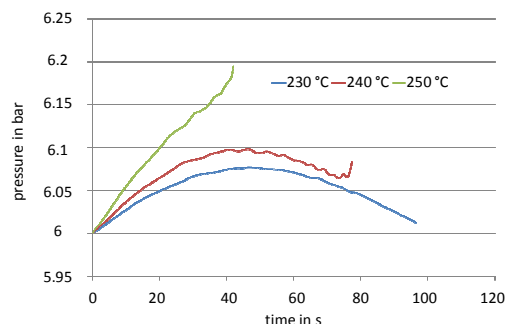

Figure 6: Simulated pressure-time curves in the vertically orientated vessel. For an initial pressure of 6 bar, the MITD was found to be 240°C (lowest wall temperature with an ignition).

Figure 7 shows the accuracy of the prediction of the MITD for the 100-dm^3-reactor in the analyzed pressure range (5-20 bar).
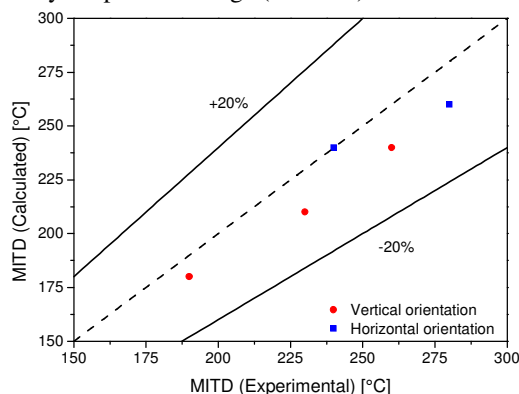

Figure 7: Accuracy of the MITD predictions.

A good agreement with the experimental results was achieved, since MITD temperatures show deviations normally under ±20%.

7 Conclusions

The ignition behavior of tetrafluoroethylene (TFE) on hot walls is a relevant topic of practical interest for the prevention of accidents in chemical plants producing polytetrafluoroethylene (PTFE). The safety related considerations of the self-heating process of TFE by the exothermic dimerization reaction to octafluorocyclobutane (OFCB) is key to understanding the mechanism which could

trigger the explosive decomposition of TFE and cause massive destruction of plant equipment or injuries to persons.

For a better understanding of the self-heating process of TFE in large scale vessels, simulations were performed COMSOL Multiphysics®. The ignition of TFE was modeled considering a heated 100-dm^3-reactor containing TFE at elevated pressures. A complex reaction scheme was used to model the self-heating process, which includes not only the dimerization reaction but also the most important side reactions. The predicted ignition temperatures were compared with experimental date, showing a good agreement. Simulations also allow for the observation of local hot spots.

8 References

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9 Acknowledgements

10 Appendix

Table 1: Governing equations.

Momentum equation	
$\rho \dfrac{\partial \vec{u}}{\partial t} + \rho(\vec{u} \cdot \nabla)\vec{u} = -\nabla p + \eta \nabla^2 \vec{u} + \vec{F}$	[Eq. 4]
Continuity equation	
$\dfrac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0$	[Eq. 5]
Heat transfer	
$\rho c_P \dfrac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) - \rho c_P \vec{u} \cdot \nabla T + S_T$	[Eq. 6]
Mass transfer	
$\dfrac{\partial C_k}{\partial t} = \nabla \cdot (D_k \nabla C_k) - \vec{u} \cdot \nabla C_k + S_{C_k}$	[Eq. 7]
Ideal gas law	
$\rho = p / (R_s T)$	[Eq. 8]

Table 2: Boundary settings for the performed simulations

	Reactor walls	Symmetry axis
Momentum equation	no slip	axial symmetry
Heat transfer	constant temperature	axial symmetry
Mass transfer	insulation	axial symmetry

Table 3: Experimental MITDs of TFE in the 100-dm^3-reactor

Vertically orientated reactor		
Set Pressure [bar]	**Initial Pressure [bar]**	**MITD Experimental [°C]**
5	6.2	260
10	10.9	230
20	22.8	190
Horizontally orientated reactor		
Set Pressure [bar]	**Initial Pressure [bar]**	**MITD Experimental [°C]**
5	5.7	280
10	11.3	240

Table 4. List of symbols

Symbol	Description	Unit
C_k	Mass concentration	mol/m^3
c_P	Specific heat	J/(kg·K)
D_k	Diffusion coefficient of the species k	m^2/s
$\vec{F}$	Buoyancy force	N/m^3
L	Length	m
p	Pressure	Pa, bar
R_s	Specific gas constant	J/(kg·K)
S_{C_k}	Species k production rate	mol/(m^3·s)
S_T	Heat production term	W/m^3
T	Temperature	K, °C
t	Time	s
$\vec{u}$	Velocity field vector	m/s
ΔH_R	Heat of reaction	J/mol
η	Dynamic viscosity	Pa·s
λ	Heat conduction coefficient	W/(m·K)
ρ	Density	kg/m^3
Ø	Diameter	m